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Electromagnetic interference shielding effectiveness of polyaniline-nickel oxide coated cenosphere composite film

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ABSTRACT

The solid waste material cenosphere (fly ash, by-product of thermal power plants) was nickel oxide nanoparticle coated (NiOC, core shell structure) by chemical heterogeneous precipitation and thermal reduction method. *in situ* synthesis of polyaniline (PANI) and NiOC composite (PNiOC) was carried out at -30 ± 2 °C under nitrogen and characterized. The free standing films of as synthesized PNiOC composite were prepared by solution casting (followed by acid vapor treatment) and electromagnetic interference (EMI) shielding effectiveness (SE) was investigated in the J-band (5.8–8.2 GHz), X-band (8.2–12.4 GHz) and Ku-band (12.4–18 GHz). An average EMI SE of ~24 dB, ~27–24 dB, ~21 dB was observed for 81 ± 3 µm thicker flexible free standing PNiOC film in the J, X and Ku-band respectively. Effective EMI shielding due to absorption (SE_A) was found to be dominant for PNiOC film. Unlike PANI emeraldine salt (ES) film, the EMI shielding due to absorption (SE_A) was found more than two times higher for PNiOC film. Due to the presence of NiOC hollow microspheres in PANI, the time average power of incident electromagnetic wave decreases resulting in an increase of EMI SE (SE_A). This film can be considered as a novel coating material for various applications such as unmanned vehicles, robotic and microwave engineering to protect against EMI.

1. Introduction

Intrinsic conducting polymers (ICP) have received tremendous attention because of its useful applications in sensors, batteries, actuators, microwave absorption and electromagnetic interference shielding (EMI shielding) [1–4]. Recently, electromagnetic interference (EMI) shielding materials are in demand due to the rapid use of radio or microwave frequencies for satellite-telecommunications, military applications etc. [4,5]. Moreover, these are non-ionizing electromagnetic radiations and have a bad impact on biological systems, animals and the environment [6]. By using conducting filler in polymer foams and films, EMI shielding and reflectance can be increased. The use of ICPs and its composites for EMI shielding has many advantages over traditional metallic sheets [5]. ICPs are lightweight, flexible and easy to synthesize [1,3,5,7]. The advantages of polyaniline over the ICPs are tuneable conductivity, adjustable permittivity/permeability, easy synthesis, low density, non-corrosiveness, good thermal and environmental stability [5,8–10]. In case of normally synthesized PANI, the presence of cross-linking is high, the conductivity is less and solution processing is difficult. The solution processing of PANI can be performed in emeraldine base form (EB, semiconductor, which becomes conductor under protonic acid doping and converts to emeraldine salt) by using *N*-methyl-2-pyrrolidone (NMP) and dimethyl-propylene urea (DMPU). However, DMPU is believed as a better solvent [11,12].

Cenospheres, the by-products of power generating thermal plants, are considered as solid wastes and causes environmental pollution. Typically, these are hollow ceramic microspheres having alumina and silica as major constituents and are light-weight, low density and nontoxic. Moreover, it is highly dispersive in the polymer matrix [13–17]. Metal – cenosphere core shell has been proposed for many potential applications [13–20]. Many techniques have been employed for coating of cenosphere, e.g. magnetic sputtering, electroless plating, physical vapour deposition, sol-gel and heterogeneous precipitation thermal reduction method [17–20]. Heterogeneous precipitation results in homogenous unit distribution and requires inexpensive reactants. Surface treatment of cenosphere is important for microwave absorption; metal (Cu) deposited cenospheres have been reported for large band width (~2 GHz) microwave absorption at a minimum thickness (~0.7 mm) [21]. As conducting polymer, porous or hollow microsphere based composites are well known for microwave absorption, therefore

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PANI-cenosphere based systems has drawn attraction for microwave absorption as well as EMI shielding [22]. Magnetic nanoparticles coated cenospheres (core shell structure) i.e., soft magnetic microspheres have been reported as most suitable for microwave absorption [20,22]. However, most of the studies were carried out for powder pressed samples having thickness more than 2 mm. Recent advances in microwave engineering demands lightweight flexible thin films for microwave absorption and EMI shielding [4,5,11].

Nickel oxide (NiO) nanoparticles have been proposed for many potential applications including dielectrics [23,24]. The tremendous attention towards NiO nanoparticle is due to its superparamagnetic behaviour at room temperature and dielectric loss. Recently, it is reported that a.c. conductivity of polyaniline increases in the presence of NiO nanoparticle (especially at high frequency), which is also an important parameter for enhancing electromagnetic wave absorption [3,22]. The objective of the present work is the study of EMI shielding mechanism of multiphase nanocomposites (polyaniline -nickel oxide -cenosphere) in terms of the contribution of effective absorption and reflection to the total EMI shielding effectiveness.

2. Experimental

2.1. Chemicals

Cenospheres were obtained from National Thermal Power Corporation (NTPC), India, with particle size range of 15–70 µm. These were separated by using 50 µm sieve. Other chemicals used (AR grade) were procured from local suppliers.

2.2. Pretreatment of cenospheres

The cenospheres were cleaned before use. Typically, 5 g of FAC was dispersed in 5% NaOH solution followed by stirring with 1 M mixture of nitric acid (HNO_3) and sulphuric acid (H_2SO_4) at 3:1 ratio for 3 h at room temperature. Obtained precipitates were washed several times with deionised water and dried at 110 °C for 12 h.

2.3. Chemical synthesis of NiO coated cenosphere

Cleaned cenosphere was nickel oxide functionalized by heterogeneous precipitation thermal reduction method. Firstly, 2 g cenosphere were dispersed in 120 ml of PEG 800 (2 g) suspended aqueous solution. 0.5 M nickel nitrate solution ($Ni(NO_3)_2{\cdot}6H_2O$) and 1 M ammonium bicarbonate (NH_4HCO_3) solution were gradually added at 3 ml/min (pH was maintained at 7~8). The solution was kept for stirring for 6 h at room temperature. The obtained precipitate was filtered and washed several times with deionised water and kept in oven at 80 °C for 12 h. Secondly, thermal reduction of this precursor was done at 600 °C for 3 h.

2.4. *in situ* synthesis of PANI-NiO-cenosphere composite

in situ synthesis of PANI-NiO-cenosphere (PNiOC) and PANI-cenosphere (PC) composites were carried out in nitrogen by oxidative polymerization of aniline in an immersion cooler (Julabo) [28]. Aniline was purified by immersing KOH pellets and then double distilled. 1 g of as prepared NiO-cenosphere was dispersed in 80 ml of 1 M HCl solution and 10 ml aniline was mixed at -30 ± 2 °C. To reduce the freezing temperature 6 M LiCl was added. Then the pre-cooled solution of ammonium persulphate (APS, 0.6 M) also in HCl (1 M, 80 ml), LiCl (6 M) was added at the rate of 3 ml/min using an external pump to the aniline solution. The reaction was allowed to proceed for 6 h at -30 ± 2 °C. The resulting precipitate was washed repeatedly with deionised water and deprotonated by stirring in 4 wt. % ammonia solution for 8 h at room temperature. The obtained composite precipitate was again washed with deionised water and methanol repeatedly. Finally it was kept in vacuum oven at 50 °C for 12 h. Similarly PANI-cenosphere and PANI were also synthesized under the same conditions.

2.5. Preparation of PANI-NiO-cenosphere composite film

Under stirring, 4 wt. % of synthesized PNiOC composite powder was added very slowly to the DMPU solvent. This mixture was further stirred for 5 h. The resulting solution was poured on to glass moulds and placed into an oven under a dynamic vacuum of 400 mm Hg at 70 °C for 12 h. Thus resulting films were acid vapor treated (1 M HCl) under vacuum for 72 h to achieve stable conductivity. Finally, it was dried under ultra-pure nitrogen. Similarly PANI-cenosphere (PC) and polyaniline film (PANI ES) was also prepared. The average thicknesses of PANI ES, PC and PNiOC films were found 84 ± 2 µm, 80 ± 3 µm and 81 ± 3 µm respectively.

2.6. Characterizations

The synthesized samples were coated over carbon tape, sputter coated with gold and surface morphologies were examined by using high resolution FESEM (Carl Zeiss). The PANalytical X-ray diffractometer was used for collecting crystallographic data and crystallite size determination by using Cu K_α radiation ($\lambda = 1.540598$ Å) in scattering range (2θ) of 10–80° with a scan rate of 0.06°/sec and slit width of 0.1 mm. The magnetic properties were investigated at room temperature by using a vibrating sample magnetometer (Lake Shore, Inc.). EMI SE measurement was carried out by using Agilent NS230A vector network analyzer. Thru-Reflect-Line (TRL) calibration was performed in the J-band (5.8–8.2 GHz), X-band (8.2–12.4 GHz) and Ku-band (12.4–18 GHz) before taking the measurements[25]. Three trials of each sample film was carried out by clamped tightly between two coaxial waveguide adapters and the *S*-parameters, S_{11} and S_{21}, were measured.

3. Results and discussion

3.1. Characterization of PANI-NiO-cenosphere composite

The surface morphology of cleaned cenosphere and NiO-cenosphere composite is shown in Fig. 1. The cenospheres are spherical hollow microspheres [17,22]. As shown in Fig. 1**(c)** and **(d),** surface morphology of NiO-cenosphere shows that NiO nanoparticles were coated over cenosphere surfaces almost homogenously. However, some small agglomerated regions were also observed and is believed to be due to the magnetic dipole-dipole interaction between NiO nanoparticles as cenosphere is non-magnetic [20,22]. In case of defect bearing cenospheres the agglomerated regions are more prominent [22].

The obtained X-ray diffraction (XRD) patterns of NiO-cenosphere, PANI, PANI-NiO-cenosphere composites are shown in Fig. 2**(a)**. The characteristic diffraction peaks of NiO-cenosphere at 2θ values of 37.53°, 43.71, 63.51° and 76.10° correspond to (111), (200), (220) and (311) planes of NiO respectively. It was observed that the (200) plane of nickel oxide is the most intense. It is due to the minimum specific free energy of NiO at (200). The crystallite size was estimated from full width half maxima (FWHM) of the (200) plane by using Scherrer formula [26] and it was found ~32 nm. The XRD pattern of PANI shows the amorphous nature and wide diffraction peaks were observed at ~15° and ~25° corresponds to periodicity (parallel and perpendicular) and the lower coherence length of PANI [27,28]. The obtained XRD patterns of composite sample (PNiOC) suggest the semi crystalline nature, both the NiO-cenosphere and PANI diffraction peaks were observed.

The magnetic properties of NiO-cenosphere and PANI-NiO-cenosphere composites were measured at 300 K and the obtained magnetization curves are shown in Fig. 2**(b)**. The NiO-cenospheres and PANI-